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(54) Paper coating pigments, coated paper and method of gravure printing.

(57) A pigment for a paper coating composition contains a layer lattice silicate which has a relatively narrow range of particle size distribution compared with pigments of conventional paper coating compositions, and which includes not more than 5%, by weight, of particles which have an equivalent spherical diameter of less than 0.25 microns.

Paper coated with a composition including the pigment provides good results when printed by a gravure process.

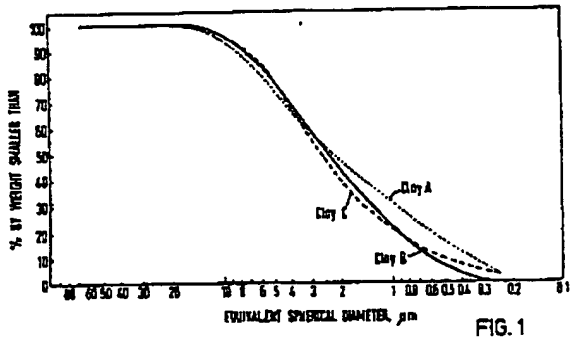

FIG. 1

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TITLE MODIFIED
see front page.

PAPER COATING PIGMENTS

FIELD OF THE INVENTION

This invention relates to pigments for paper coating, particularly, although not exclusively, to pigments for use in the manufacture of lightweight coated paper for gravure printing.

BACKGROUND OF THE INVENTION

Gravure printing is a form of intaglio printing, i.e. printing which uses a plate or cylinder into the surface of which the subject matter to be printed is etched or engraved. A liberal film of fluid printing ink is applied to the whole printing surface and the surface is then wiped, for example by a doctor blade, in order to remove all the ink from the unindented parts of the surface leaving ink only in the indentations or cells. Paper in a continuous web or in separate sheets is then pressed into contact with the inked surface in order to receive an impression of the subject matter.

In the most widely used kind of gravure printing, which is known as the rotogravure process, the subject matter, which may be textual or pictorial, is etched into the printing surface in the form of a matrix of cells which vary in depth and/or in surface area, so that the cells corresponding to the darker parts of the subject matter have a greater capacity for ink than the cells which correspond to the lighter parts of the subject matter. An image of the subject matter is formed by a photographic process on a sheet of carbon tissue which is impregnated with gelatine containing a light sensitive reagent. There is first formed on the sheet of carbon tissue a

rectilinear-grid having from 59 to about 160 lines to the centimetre. The grid is formed by placing a screen consisting of small opaque squares separated by fine transparent lines in contact with the impregnated carbon tissue and exposing the screen to light so that the gelatine in the tissue immediately below the lines is rendered insoluble.

The image of the subject matter to be printed is then superimposed on the image of the screen by placing in contact with the carbon tissue a positive photographic transparency of the subject matter-for the colour to be printed and exposing the transparency to light. Again the gelatine in areas of the carbon tissue lying immediately beneath clear areas of the transparency is rendered insoluble and in other areas the solubility of the gelatine is inversely proportional to the amount of light transmitted by the transparency. The carbon tissue is then placed over the surface of a specially prepared copper roller, those parts of the gelatine which are still soluble are washed away, and the surface of the roller is etched with a suitable reagent such as ferric chloride. The result is that the surface of the cylinder is etched in a pattern composed of a very large number of cells defined by a rectilinear grid, the depth of the cells in a particular area being dependent on the solubility of the gelatine in the carbon tissue overlying that area and thus on the amount of light transmitted through the transparency in that area.

The choice of a suitable paper for gravure printing is largely empirical. Good results can be obtained on a wide variety of different types of paper ranging from newsprint to the finest matt art paper. However as a general rule, the paper should be absorbent enough to take the ink without the exertion of undue pressure, and a coated paper is generally required for the best results.

The gravure printing process is especially suitable for printing runs in which a large number of copies are reqired

because the recessed cells of a gravure cylinder are less subject to wear through abrasion than the relief type of the letterpress process.

The process is therefore used for printing magazines, mail order catalogues and other periodical publications having a large circulation. There is an increasing trend to print this type of publication on a lightweight coated paper in order to minimise postal costs. Unfortunately a very common defect which appears when subject matter is printed by gravure on lightweight coated papers is a speckled effect which is most noticeable in the middle tones. This effect is caused by poor contact between the surface of the paper and the surface of the cylinder so that the ink is not drawn out from some of the cells with the result that some of the minute dots which make up the printed image are missing.

BRIEF DESCRIPTION OF THE PRESENT INVENTION

According to the present invention there is provided a pigment for a paper coating composition, which pigment consists predominantly of a layer lattice silicate with a particle size range factor (as hereinafter defined) which is less than 3, not more than 5% of the particles by weight having an equivalent spherical diameter which is less than 0.25 microns.

The present invention also provides a method of preparing a pigment as just defined, a paper coating composition including the pigment, and a method of gravure printing comprising printing onto paper coated with the coating composition.

The particle size range factor (PSRF) provides an indication of the range of particle sizes in the pigment as a function of the median particle size. It is defined as follows:

$$PSRF = \frac{e.s.d._{90\%} - e.s.d._{10\%}}{e.s.d._{50\%}}$$

where $e.s.d._{90\%}$, $e.s.d._{10\%}$ and $e.s.d._{50\%}$ are the equivalent spherical diameters below which fall 90%. 10% and 50% respectively of the particles, by weight.

As stated, a pigment in accordance with the invention consists predominantly of a layer lattice silicate. Preferably, the layer lattice silicate constitutes at least 70% of the pigment, and it may constitute substantially the whole of the pigment.

The present invention is based on the discovery that the "printability" of a coated paper by gravure methods can be significantly enhanced by reducing the range of particle sizes in the pigment, and by reducing the proportion of finer particles.

Thus, when a graph is plotted with the logarithm of the equivalent spherical diameter as the abscissa and "% by weight finer than" as the ordinate, the central portion of the resulting sigmoid curve is steeper for a pigment in accordance with the present invention than it is for a conventional pigment and the length of the "tails" of the curve, especially that at the fine particle size end is reduced as compared with the case for conventional pigments.

By the length of the tails of the curve we mean the distance over which the flatter top and bottom portions of the sigmoid curve approach the "100% by weight finer than" and the "0% by weight finer than" ordinates respectively. The pigment having a particle size distribution of reduced range may be produced, for example, by subjecting a wider-range grade of the layer lattice silicate to one or more additional particle size separations, or by grinding a coarse residue grade of the layer lattice silicate with a particulate grinding medium in aqueous suspension, or by a combination of these methods.

The additional particle size separations will generally be such as to remove the finest particles in

the distribution of particle sizes. For example, in many cases good results are obtained if substantially all particles having an equivalent spherical diameter smaller than 0.25 micron are removed. The particle size separations may be performed by gravitational sedimentation of a deflocculated aqueous suspension of the layer lattice silicate, but since a very long time is required to effect a separation at such a fine particle size by this method it is convenient to use a centrifuge such as a scroll discharge centrifuge or a nozzle discharge disc centrifuge.

The particle size separations may also serve to remove substantially all particles larger than, say, 5 microns or 2 microns.

The grinding of the coarse residue grade of the layer-lattice silicate is conveniently performed using a particulate grinding medium comprising particles of sizes in the range from 0.2 mm to 2.0 mm. Most preferably the particulate grinding medium consists of particles in the size range from 0.5 to 1.0 mm. The coarse residue grade of the mineral material generally contains less than 20% by weight of particles having an equivalent spherical diameter smaller than 2 microns.

The layer lattice silicate is most preferably a kaolinitic clay but alternatively talc, or a mixture of talc and kaolinitic clay, may be used. The layer lattice silicate preferably has a particle size distribution such that

substantially all the particles are smaller than 50 microns.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention is illustrated by the following Examples, in which reference is made to the accompanying Figures. In these Figures:

Figure 1 shows particle size distribution curves for three kaolinitic clays "A", "B" and "C", and

Figure 2 shows particle size distribution curves for three further kaolinitic clays "D", "E" and "F".

DETAILED DESCRIPTION OF THE INVENTION WITH REFERENCE TO EXAMPLES

Clay "A" was prepared by subjecting a deflocculated aqueous suspension of raw clay from Cornwall to a particle size separation to remove substantially all particles larger than 50 microns.

The particle size distribution of clay "A" may be indicated by the following parameters:-

½ by weight larger than 10 microns equivalent spherical diameter (e.s.d.)	6%
% by weight smaller than 2 microns e.s.d.	46%
% by weight smaller than 1 micron e.s.d.	31%
e.s.d.$_{90\%}$	8.3 microns
e.s.d.$_{50\%}$	2.25 microns
e.s.d.$_{10\%}$	0.38 microns
PSRF	3.52

Clay "B" was prepared by subjecting clay "A" in a deflocculated aqueous suspension to a second particle size separation in a nozzle discharge disc centrifuge to remove substantially all particles smaller than 0.25 micron.

The particle size distribution of clay "B" may be indicated by

the following parameters:-

% by weight larger than 10 microns e.s.d.	5%
% by weight smaller than 2 microns e.s.d.	44%
% by weight smaller than 1 micron e.s.d.	22%
$e.s.d._{90\%}$	7.0 microns
$e.s.d._{50\%}$	2.35 microns
$e.s.d._{10\%}$	0.63 microns
PSRF	2.72

Clay "C" was prepared by subjecting a coarse, residue kaolin to attrition grinding in aqueous suspension with silica sand of grain size 0.5 - 1.0 mm. The suspension of ground kaolin was deflocculated and subjected to a particle size separation in a nozzle discharge disc centrifuge to remove substantially all of the particles having an equivalent spherical diameter smaller than 0.25 micron. The suspension of kaolin, free from ultrafine particles, was then flocculated and dewatered by filtration, and the filter cake was pugmilled, 40 horsepower hours of energy per ton of dry kaolin (160 $kJ.kg^{-1}$) being dissipated in the kaolin.

The particle size distribution of clay "C" may be indicated by the following parameters:-

% by weight larger than 10 microns e.s.d.	5%
% by weight smaller than 2 microns e.s.d.	39%
% by weight smaller than 1 micron e.s.d.	20%
$e.s.d._{90\%}$	7.1 microns
$e.s.d._{50\%}$	2.65 microns
$e.s.d._{10\%}$	0.56 microns
PSRF	2.47

Clay "D" was prepared by subjecting a clay of the same type as clay "A" to a particle size separation in deflocculated aqueous suspension in a scroll discharge centrifuge in order to remove substantially all particles having an equivalent spherical diameter larger than 5 microns.

The particle size distribution of clay "D" may be indicated by the following parameters:-

% by weight larger than 5 microns e.s.d.	1%
% by weight smaller than 2 microns e.s.d.	83%

% by weight smaller than 1 micron e.s.d.	64%
$e.s.d._{90\%}$	2.6 microns
$e.s.d._{50\%}$	0.74 microns
$e.s.d._{10\%}$	0.2 microns
PSRF	3.24

Clay "E" was prepared by subjecting clay "C" to a first particle size separation in deflocculated aqueous suspension in a scroll discharge centrifuge to remove substantially all particles having an equivalent spherical diameter larger than 2 microns and then to a second particle size separation in a nozzle discharge disc centrifuge to remove sustantially all particles having an equivalent spherical diameter smaller than 0.25 micron.

The particle size distribution of clay "E" may be indicated by the following parameters:-

% by weight smaller than 2 microns e.s.d.	95%
% by weight smaller than 1 micron e.s.d.	92%
% by weight smaller than 0.25 micron e.s.d.	3%
$e.s.d._{90\%}$	0.96 microns
$e.s.d._{50\%}$	0.55 microns
$e.s.d._{10\%}$	0.32 microns
PSRF	1.16

Clay "F" was prepared by subjecting clay "D" in deflocculated aqueous suspension to a particle size separation in a scroll discharge centrifuge to remove substantially all particles having an equivalent spherical diameter smaller than 1 micron.

The particle size distribution of clay "F" may be indicated by the following parameters:-

% by weight larger than 5 microns e.s.d.	5%
% by weight smaller than 2 microns e.s.d.	35%
% by weight smaller than 1 micron e.s.d.	1%
$e.s.d._{90\%}$	3.7 microns
$e.s.d._{50\%}$	2.3 microns
$e.s.d._{10\%}$	1.5 microns
PSRF	0.96

A further clay "G" was prepared as follows.

A suspension of a coarse residue kaolin was subjected to attrition grinding with a particulate grinding medium comprising silica sand of grain size in the range 0.5 to 1.0 mm to give a comminuted product having a particle size distribution such that 11% by weight consisted of particles having an equivalent spherical diameter larger than 10 microns and 28% by weight consisted of particles having an equivalent spherical diameter smaller than 2 microns. The suspension of the comminuted product was screened through a No. 300 mesh B.S. sieve (nominal aperture 53 microns), diluted to a solids content of 14.6% by weight, treated with sufficient sodium hydroxide to raise the pH to 8.0 and with 0.3% by weight, based on the weight of dry kaolin, of a sodium polyacrylate dispersing agent in order to deflocculate the kaolin, and passed through a scroll discharge centrifuge at a flow rate such that substantially all particles having an equivalent spherical diameter smaller than 0.25 micron were separated from the suspension. The coarser product from the centrifuge was then diluted with water, flocculated with sulphuric acid, dewatered by filtration and thermal drying to a moisture content of about 25% by weight and subjected to pugmilling under conditions such that 79.5 kJ of energy per kg. of dry kaolin was dissipated in the moist kaolin. The pugmilled kaolin was designated "Clay G".

The particle size distribution of Clay "G" may be indicated by the following parameters.

% by weight larger than 10 microns e.s.d.	6%
% by weight smaller than 2 microns e.s.d.	32%
% by weight smaller than 1 micron e.s.d.	14%
$e.s.d._{90\%}$	8.0 microns
$e.s.d._{50\%}$	3.2 microns
$e.s.d._{10\%}$	0.84 micron
PSRF	2.24

As a further example, talc was beneficiated by crushing, grinding, froth flotation to remove magnesite,

further grinding in the wet state in ball mills, claissification in hydraulic cyclones, filtration, drying and final comminution in a fluid energy mill to give a product having the following particle size parameters:-

% by weight larger than 10 microns e.s.d.	9%
% by weight smaller than 2 microns e.s.d.	32%
% by weight smaller than 1 micron e.s.d.	13%
$e.s.d._{90\%}$	9.3 microns
$e.s.d._{50\%}$	3.25 microns
$e.s.d._{10\%}$	0.82 micron
PSRF	2.61

Each clay was incorporated in turn into a paper coating composition prepared according to the following recipe:-

Ingredient	Parts by weight
Clay	100
Sodium polyacrylate dispersing agent	0.3
Self-thickening acrylic copolymer latex adhesive	4.8
Sodium hydroxide to pH 9	
Water to a viscosity of 1500 centipoise as measured on a Brookfield viscometer at 100 rpm.	

The beneficiated talc was mixed with water containing, as dispersing agents for the talc, 0.5% by weight, based on the weight of talc, of sodium hexametaphosphate and 2.0% by weight, based on the weight of talc, of the nonionic, low-foaming surfactant known as "PLURONIC L62" (Trade Mark of Wyandotte Chemicals Corporation). "PLURONIC L62" has a hydrophilic portion consisting of polyethylene oxide groups and a hydrophobic portion consisting of a polyoxypropylene base of approximate molecular weight 1750. The proportion of polyethylene oxide groups is approximately 20% by weight based on the weight of the polyoxypropylene base.

In order to form a paper coating composition the deflocculated suspension of talc was mixed with 4.8 parts by weight of a self-thickening acrylic copolymer latex

adhesive per hundred parts of talc and sufficient sodium hydroxide to raise the pH to 9. The paper coating composition contained 54.9% by weight of solids and had a viscosity of 680 centipoise at 22°C as measured on a Brookfield viscometer at 100 rpm.

Each coating composition was coated at various different coating weights on to a lightweight coating base paper using a laboratory coating maching of the type described in British Patent Specification No. 1,032,536 running at a speed of 750 metres per minute for compositions containing clays A to F and of 400 metres per minute for compositions containing clay "G" and beneficiated talc. The batches of coated paper were calendered with 10 passes at a line pressure of 375lb. per linear inch (67 kg. per cm.) and at 65°C.

Small samples were cut from each batch of coated paper and were tested for gravure printing quality on a Winstone gravure proofing press as described in the article "Realistic paper tests for various printing processes" by A. Swan published in 'Printing Technology" Vol 13, No. 1, April 1969, pages 9-22. The Winstone proofing press comprises a rotating printing cylinder on which are etched an area which will print solid black and two areas which will print a light grey tone, these last two areas differing in the etching process which is used. The proofing press is also provided with a pan for ink, a doctor blade, an impression cylinder, means for pressing the impression cylinder against the printing cylinder, means for drying the printed impression and feed and take-up rolls for a web of backing paper.

The pan for ink may be raised by a lever mechanism to bring the ink contained in the pan into contact with the lower part of the printing cylinder. The doctor blade has a thickness of 0.13 mm, projects 5.0 mm beyond a supporting backing blade and is mounted in a position such that, as

the printing cylinder rotates, it wipes away all the ink from the unindented parts of the surface of the cylinder leaving ink only in the cells. The ink used is based on xylene and should have a viscosity such that a standard Ford No. B4 flow cup viscometer empties in 50 seconds. The impression cylinder is covered with rubber of 65° Shore hardness and is pressed against the printing cylinder by a small pneumatic ram operating at a pressure of 60 psig (414 kPa).

The small samples of coated paper are attached by adhesive tape to the web of backing paper which passes from the feed roll, through the nip between the printing cylinder and the impression cylinder, under a radiant heat dryer and over a jet of warm air to dry the printed impression before reaching the take-up roll.

In operation, enough of the backing paper is unrolled to feed through the complete assembly to the take-up roll. This length is normally 3 metres and a line is drawn on the backing roll in this position. Starting from the line, positions for mounting the sample of paper are marked off using a template which ensures that the samples are spaced at distances equal to the circumference of the printing cylinder so that each receives an identical impression. The samples of paper are mounted on the backing paper which is wound back on to the feed roll. The free end of the backing paper is threaded through the assembly to the take-up roll and the line drawn on the backing paper is registered to a reference line on the printing cylinder.

The printing and impression cylinders are then set into rotation until all the samples of paper have been printed. The printed samples are compared with reference samples which are graded from 1 to 7 according to the degree of speckle or the number of missing dots per square centimeter. Grade 1 is the best result and grade 7 the worst.

From the samples of paper coated at different coat weights for each of the eight pigments the results corresponding to coat weights of 8 $g.m^{-2}$ and 10 $g.m^{-2}$ were

found by interpolation.

The results are set forth in the following Table.

TABLE

Material	Print grade at 8 g.m.$^{-2}$ coat weight	Print grade at 10 g.m.$^{-2}$ coat weight
Clay A	4½	3
Clay B	1½	1
Clay C	2	1½
Clay D	3½	2
Clay E	1½	1
Clay F	2	1
Clay G	1½	1½
Beneficiated Talc	1½	1½

It will be seen that in each case paper coated with the clays according to the invention "B", "C", "E", "F", "G" and with beneficiated talc gives gravure prints having fewer missing dots per square centimeter than paper coated with clays "A" and "D", and the improvement is especially noticeable at the lighter coat weight.

It is not at present clear to us why clays "B", "C", "E", "F" and "G" and the beneficiated talc give better results than clays "A" and "D". The presently preferred theory, however, is that clays "B", "C", "E", "F" and "G" and the beneficiated talc provide a more compressible coating than clays "A" and "D", and this results in better take-up of ink from the cells of the etched cylinder. The compressibility is a result of the relatively poor packing characteristics of clays "B", "C", "E", "F" and "G" and the beneficiated talc which in turn is a consequence of the uniform particle size distribution of these materials.

CLAIMS

1. A pigment for a paper coating composition, which pigment consists predominantly of a layer lattice silicate, characterized in that the layer lattice silicate has a particle size range factor (as hereinbefore defined) which is less than 3, and in that not more than 5% of the particles, by weight, have an equivalent spherical diameter which is less than 0.25 microns.

2. A pigment as claimed in claim 1, characterized in that the particle size range factor is less than 2.

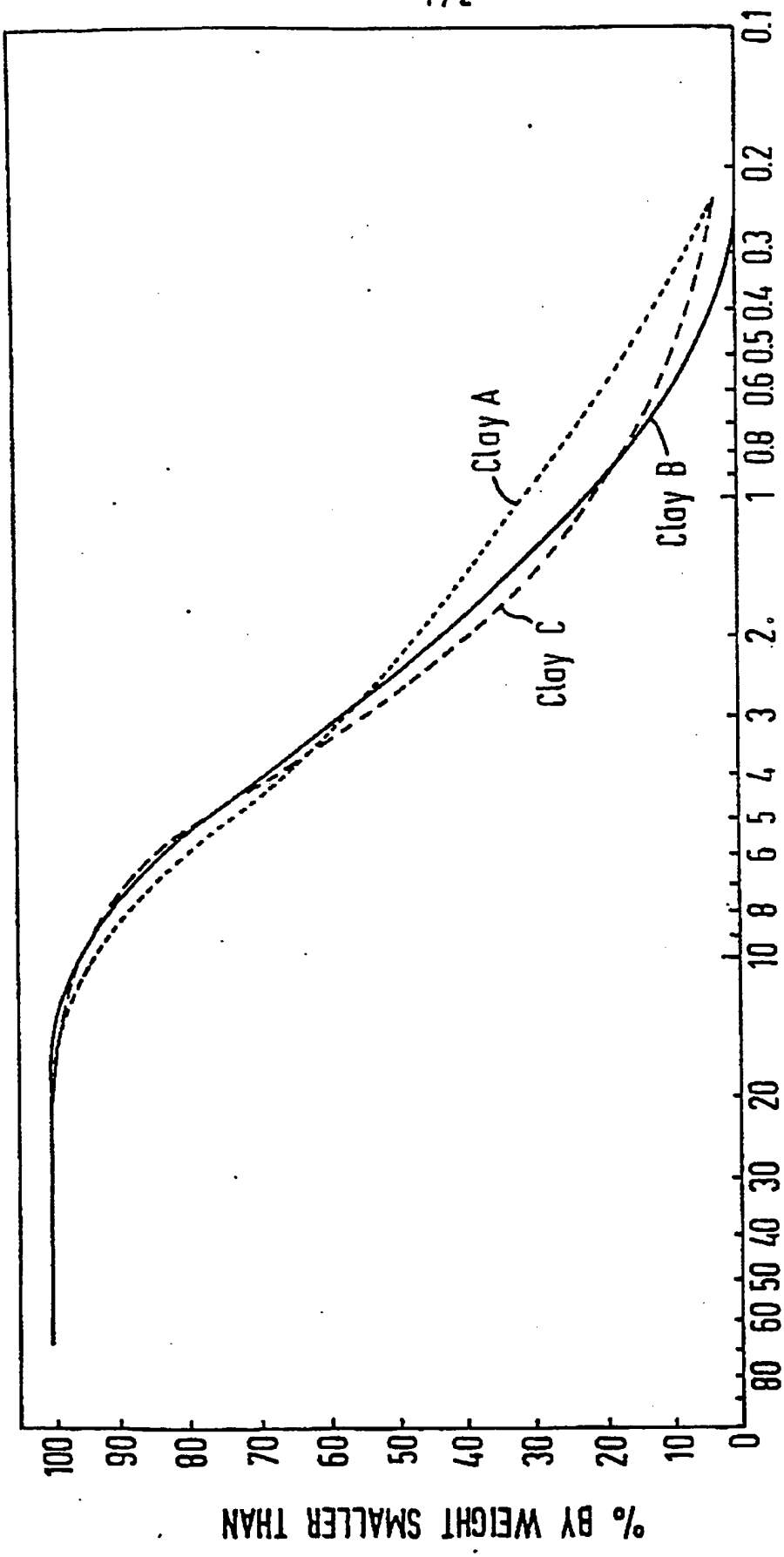
3. A pigment as claimed in claim 1 or 2, characterized in that the layer lattice silicate is kaolinitic clay or talc.

4. A pigment as claimed in any one of claims 1 to 3, characterized in that the layer lattice silicate is white.

5. A paper coating composition, characterized in that it includes a pigment in accordance with any one of the preceding claims.

6. Paper, characterized in that it is provided with a coating composition in accordance with claim 5.

7. A method of gravure printing, characterized in that printing takes place onto paper in accordance with claim 6.


% BY WEIGHT SMALLER THAN
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90
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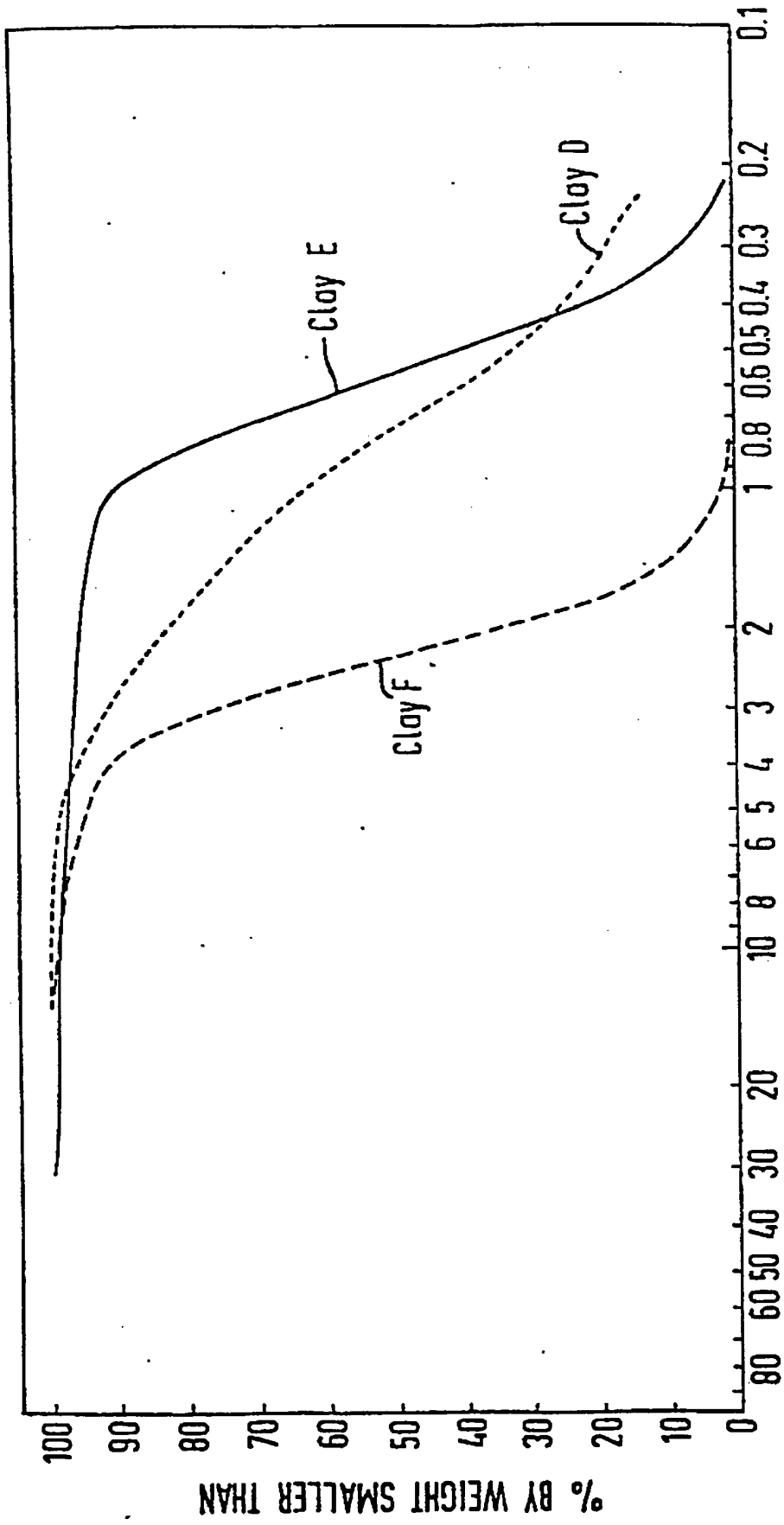
70
60
50
40
30
20
10
0
80 60 50 40 30 20 10 8 6 5 4 3 2 1 0.8 0.6 0.5 0.4 0.3 0.2 0.1
EQUIVALENT SPHERICAL DIAMETER, μm
Clay A
Clay B
Clay C

FIG. 1


% BY WEIGHT SMALLER THAN
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70
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50
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30
20
10
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80 60 50 40 30 20 10 8 6 5 4 3 2 1 0.8 0.6 0.5 0.4 0.3 0.2 0.1
EQUIVALENT SPHERICAL DIAMETER, μm.
Clay E
Clay D
Clay F

FIG. 2

European Patent Office

EUROPEAN SEARCH REPORT

Application number
EP 80 30 3209

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.³)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	US - A - 2 524 816 (S.C. LYONS) * Column 1, line 1 - column 2, line 6; column 3, lines 3,4, 55-75; column 4, line 1 - column 6, line 20; figure 3 * --	1,3-6	D 21 H 1/22 B 41 M 1/10
	US - A - 2 158 987 (W.T. MALONEY) * Page 1, left-hand column, line 1 - page 2, left-hand column, line 34; page 2, right-hand column, line 70 - page 3, right-hand column, line 9 * --	1,3-6	TECHNICAL FIELDS SEARCHED (Int. Cl.³) B 41 M 1/10 1/36 C 04 B 33/04 D 21 H 1/22
	US - A - 1 934 642 (H.R. RAFTON) * Page 1, left-hand column, line 1 - right-hand column, line 95; page 3, left-hand column, lines 3-71 * --	1,3-6	
	GB - A - 2 015 487 (PLUSS-STAUFER) * Claims 1-8,13 * ----	1,3-6	

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	18-12-1980	NESTBY

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